PB82-196353

Determination of Chemical Residues in Whole Blood of Selected Love Canal Area Residents

(U.S.) Health Effects Research Lab.
Research Triangle Park, NC

Prepared for

Department of Justice
Washington, DC

24 Jun 80

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

EPA-600/1-80-036
September 1980

PB82-196353

EPA

Research and Development

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TECHNICAL REPORT DATA *(Please read Instructions on the reverse before completing)*		
1. REPORT NO. EPA-600/1-80-036	2.	3. RECIPIENT'S ACCESSION NO. PB82 196353
4. TITLE AND SUBTITLE Determination of Chemical Residues in Whole Blood of Selected Love Canal Area Residents		5. REPORT DATE September 1980 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Analytical Chemistry Branch Environmental Toxicology Division		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Analytical Chemistry Branch Environmental Toxicology Division HERL,USEPA Research Triangle Park, NC 27711		10. PROGRAM ELEMENT NO. 1EA615 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Office of Research and Development (RTP,NC) Health Effects Research Lab US EPA Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE 600/11
15. SUPPLEMENTARY NOTES Project Officer: Robert G. Lewis Telephone: 541-2510		

16. ABSTRACT

This paper contains the results of the analysis of blood samples collected fron residents of the Love Canal vicinity of Niagara Falls, New York, for residues of certain toxic chemicals. The original list of chemicals reviewed contained a total of 55 chemical compounds, classes of compounds, and metals. The analyses were seen to fall into four categories: I. Elemental, II. Volatile Organics, III. Non-volatile Neutral Organics, and IV. Acidic Organics. Further analyses would be needed to better define the utility of exposure assessment using these chemical measurements because the residue levels encountered by this study were very low.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Love Canal Chemical residue Blood		06T
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED 20. SECURITY CLASS *(This page)* UNCLASSIFIED	21. NO. OF PAGES 40 22. PRICE

EPA Form 2220-1 (9-73)

EPA-600/1-80-036
September 1980

DETERMINATION OF CHEMICAL RESIDUES IN WHOLE BLOOD OF SELECTED LOVE CANAL AREA RESIDENTS

Analytical Chemistry Branch
Environmental Toxicology Division
Health Effects Research Laboratory
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

June 24, 1980

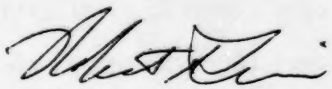
PREFACE

This report was prepared by Dr. Douglas W. Bristol, of the Analytical Chemistry Branch (ACB), who coordinated the team of researchers responsible for this work. Gas chromatographic determinations were carried out by Thomas R. Edgerton, Howard L. Crist, and Kathryn E. MacLeod. High performance liquid chromatographic analyses were conducted by Emile Lores. Mass spectrometric confirmational analyses were provided by Dr. G. Wayne Sovocool (GC/MS) and Dr. Lynn H. Wright (HPLC/MS). Diane E. Bradway assisted in the collection of the blood samples and their chain-of-custody transport from Niagara Falls, New York to Research Triangle Park. Other members of the ACB staff also assisted in these chemical analyses. Statistical analyses were performed by John Creason, Vic Hasselblad, and Violette Kasica of the Biostatistics Branch, Biometry Division, Health Effects Research Laboratory (HERL). Typing support was provided by the Word Processing Center, HERL.

Since the field samples were provided to this laboratory for analysis without closely matched, simultaneous controls, members of the Analytical Chemistry Branch donated blood specimens for the purpose of methods trial and validation studies. This volunteer blood was drawn in precisely the same manner as that taken from the field group and under the auspices of Ms. Bradway. In addition, blood samples were taken from three students of the University of North Carolina, Chapel Hill, North Carolina, in order to conduct method fortification-recovery studies.

All chemical residues found in the blood samples collected from residents of the Love Canal area (field group) were also found in the

volunteer group. Upon completion of chemical analyses of the samples, statistical analyses of the data were carried out. Caution should be exercised in comparing field and volunteer group values, however, because the volunteer group does not constitute a matched, simultaneous control group. Evaluation of the residue levels found in the field samples analyzed is very difficult because of the paucity of data relating to this approach for human exposure assessment.



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INTRODUCTION

In early January 1980, the Analytical Chemistry Branch, Environmental Toxicology Division, Health Effects Research Laboratory, Research Triangle Park, NC (ACB, ETD, HERL/RTP) was asked to analyze human whole blood samples collected from residents of the Love Canal vicinity of Niagara Falls, NY, for residues of certain toxic chemicals. The original list of chemicals reviewed contained a total of 55 chemical compounds, classes of compounds, and metals. The analyses requested were seen to fall essentially into four categories: I. Elemental, II. Volatile Organics, III. Non-volatile Neutral Organics, and IV. Acidic Organics. An alphabetical listing of the chemicals analyzed within each category, arranged according to the method of analysis employed, is presented in Appendix I. The Analytical Chemistry Branch (ACB) made arrangements with Dr. John Going of Midwest Research Institute, Kansas City, MO, to analyze samples for residues of elements and chemicals in Categories I and II (see separate report, copy attached). The analyses to be conducted by the ACB covered chemicals in Categories III and IV. The former were to be determined by familiar gas chromatographic (GC) methods (Category III, Methods A and B) and confirmed by gas chromatography/mass spectrometric (GC/MS) means (Category III, Method C). The latter were to be determined by high-performance liquid chromatography (HPLC) with electrochemical detection (ECD) (Category IV, Method A) and confirmed by the specialized technique of HPLC/MS (Category IV, Method B). Details of the actual methods employed and the results obtained are the subject of this report and supersede any and all preliminary communications of our results.

It should be noted that several substances on the original list of chemicals reviewed should not be expected to exist in blood (or any other part of the body); e.g., white phosphorus, hydrogen sulfide, and phosgene. Some of the others would be expected to be present only if significant exposure to them had occurred shortly before sampling. The more heavily chlorinated neutral organics would be best located in adipose tissue samples. The two dichlorodibenzodioxins and 2,3,7,8-TCDD would be better sought in adipose tissue (as planned separately for one sample from the same site) and require specific sample preparation which is available only at the Toxicant Analysis Center, Office of Pesticides and Toxic Substances, Bay St. Louis, MS.* For these and other reasons discussed below, the ACB did not attempt to analyze the field blood samples for all of the chemical compounds, classes of compounds, and metals on the original list of chemicals reviewed.

SAMPLING

On Friday, January 18 and Saturday, January 19, 1980, Ms. Diane Bradway, a Research Chemist on the staff of the ACB, supervised the collection of 72 duplicate blood samples (7 to 10 g each) taken from 36 residents of the Love Canal area. The samples were transported by her to the ACB, stored, and released under chain-of-custody procedures.

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*Two adipose tissue samples were taken from the Love Canal area residents at about the same time for dioxin analysis. These were processed by the Toxicant Analysis Center, incorporated into the Agency Dioxin Monitoring Program, and analyzed by capillary column gas chromatography: high resolution mass spectrometry by Robert L. Harless of the ACB. Results were negative for both samples.

Some difficulties were encountered in the sampling procedure which precluded the use of the glass syringes as originally planned. Hence, samples were drawn with heparinized BD Vacutainers®. Four Vacutainer® tubes were taken from each subject. For the purposes of the ACB analytical work, two of these were immediately transferred by the ACB chemist to separate pre-cleaned culture tubes with Teflon®-lined caps, each containing about 147 I.U. of sodium heparin, so as to minimize the contact time between the blood and rubber septum (a known source of sample contamination). These samples were frozen in dry ice for transport to RTP. The other two samples were transferred to special containers for analysis for residues of Categories I and II chemicals by a Midwest Research Institute chemist.

Efforts to analyze whole blood samples for those chemicals indicated in Categories III and IV were initiated on January 21, 1980 within the ACB. Five sub-groups were involved because of the number of methods required for complete analysis.

Closely matched, simultaneous control samples were not provided for analysis along with those taken from the 36 Love Canal area residents sampled. In order to obtain samples for method trial and validation studies, 10 volunteer whole blood samples were taken from ACB donors by a registered nurse with Vacutainers® from the same lot used to sample the Love Canal area residents and handled in the same manner as that employed at the Niagara Falls site. Later in the study, after the 36 field samples had been analyzed, approximately 50 mL glass syringe-drawn whole blood samples were obtained from three student volunteers through the cooperation of the Community Studies Division, HERL/RTP. These

volunteer samples were first analyzed for residues of Categories III and IV chemicals, then pooled, analyzed again, and partitioned for use in fortification-recovery experiments with representative chemicals in Categories III and IV.

METHODS AND RESULTS

Experimental details of the methods employed are available from the ACB; a brief outline of each method and the results obtained follow.

Category III, Method A (GC/EC-200°)

Whole blood samples (approximately 3 g) were extracted according to the procedure outlined in Section 5.A.(3) of the "Manual of Analytical Methods for the Analysis of Pesticide Residues in Human and Environmental Samples," USEPA, HERL/RTP, June 1977. After concentration to 0.5 ml, portions of each extract were analyzed by gas chromatography with electron capture detection (GC/EC) using the columns and column temperatures indicated in Chart A.

All samples were first analyzed using the OV-17/OV-210 column at 200°. The resulting chromatograms exhibited a complex sample matrix background at the very low detection limit (high sensitivity) employed. In order to avoid false positive responses or misleadingly high results, and to confirm the chemicals indicated as being present, all samples were further analyzed on the SE-30/OV-210 column unless noted otherwise. The absence of mirex was established by analysis on an OV-210 column at 200°. Selected samples were analyzed on the OV-17/OV-210 column at 175° to detect α-BHC in the presence of HCB.

CHART A

Retentions Relative to Aldrin (RRA) for Pesticides on Various Columns

Column Packing Column Temperature Pesticide	OV-17/OV-210 200° RRA	OV-17/OV-210 175° RRA	SE-30/OV-210 200° RRA
Hexachlorobenzene (HCB)	0.42	0.38	0.42
α-Hexachlorocyclohexane (α-BHC)	0.42	0.45	0.40
γ-Hexachlorocyclohexane (γ-BHC)	0.58	0.64	0.52
Pentachloronitrobenzene (PCNB)	0.63		0.54
β-Hexachlorocyclohexane (β-BHC)	0.79		0.50
δ-Hexachlorocyclohexane (δ-BHC)	0.84	0.96	0.58
Aldrin	1.00	1.00	1.00
Thiodan I	2.03		1.76
Thiodan II	3.89		2.60
Mirex	7.37		5.52
Aroclor 1260[a]	2.74		
	3.10		
	3.53		
	4.63		
	7.47		

[a]Additional peaks at RRA 1.68, 1.89, 4.05, 5.00, 6.21, and 9.89 were used to qualitatively identify Aroclor 1260.

While lower levels of each chemical being analyzed could be detected, the limit of measurement was set at that amount of each chemical required to produce a 10% full-scale recorder deflection when present in the extract of a three-gram sample. Since reagent blanks and volunteer samples did not give chromatographic peaks greater than 5% full-scale at the various retention times of interest, these analyses were performed at a signal to noise ratio of two or greater, where the noise reflects the background associated with the combined reagent and sample matrix. Because every blood sample analyzed contained HCB residue, the limit of measurement for HCB is based on the noise level associated with the reagent blank only. For Aroclor 1260, the only multi-component substance on the list of chemicals reviewed, the limit of measurement was set at that amount required to produce a 10% full scale deflection for the smallest of the five largest peaks used to quantify it (Chart A).

The results of Category III, Method A analyses for organochlorine compound residues in field samples are presented in Table I, while those in volunteer samples are presented in Table II. A summary of the Tables I and II results is presented in Table III.

Fortification-recovery study results for Category III, Method A representative chemicals that were detected as residues in whole blood samples, plus additional organochlorine pesticides, are presented in Table IV. Recovery values were obtained on five replicate whole blood volunteer samples fortified at both low and high levels (about 1 and 10 ng/g or ppb, respectively). Since the average percent recoveries for the low and high level fortifications were similar in magnitude and exhibited no definitive trend towards concentration dependency, an

overall average percent recovery based on the ten samples studied was calculated for each compound and used to correct the residues reported in Tables I, II, and III (corrected residue = residue found x 100/overall percent recovery for that compound). The overall average percent recovery values were also used to correct the limits of measurement reported in Tables I and II (limit of measurement = limit found x overall percent recovery for particular compound/100). A recovery value for Aroclor 1260 was not determined since only 1 of 48 samples exhibited a measurable residue. Based on unrelated ACB work with human serum, the recovery of Aroclor 1254 through this method is about 60%. By analogy, the corrected value for the Aroclor 1260 residue reported for field sample ACB number 119-031 in Table I would be 13 ng/g (ppb).

Category III, Method B (EC/GC-100°)

The same whole blood sample extracts subjected to Category III, Method A analysis were analyzed at lower column temperatures by GC/EC using the columns and temperatures indicated in Chart B. The support bonded-PEGS/DEGS column was used for confirmation of compounds only through 1,2,3-TCB since very few responses were observed for the higher chlorinated compounds on the OV-17/OV-210 column. The DC-200 column was useful only in confirming the presence or absence of 1,2-DCB and only 9 sample extracts were analyzed on it. The assignment of responses occurring near the RRT for 1,2-DCB and α-CT to 1,2-DCB was positively confirmed by GC/MS analysis; α-CT is not expected to be stable in blood since it decomposes in aqueous solution.

CHART B

Retentions Relative to 1,3,5-Trichlorobenzene (RRT) on Various Columns

Column Packing Column Temperature Organochlorine compound	OV-17/OV-210 100° RRT	SB-PEGS/DEGS 110° RRT	DC-200 100° RRT
1,3-Dichlorobenzene (1,3-DCB)	0.49	0.60	0.43
1,4-Dichlorobenzene (1,4-DCB)	0.53	0.68	0.44
α-Chlorotoluene (α-CT)	0.60	0.96	0.43
1,2-Dichlorobenzene (1,2-DCB)	0.63	0.85	0.51
2,4-Dichlorotoluene (2,4-DCT)	0.98	0.99	
1,3,5-Trichlorobenzene (1,3,5-TCB)	1.00	1.00	1.00
Hexachloro-1,3-butadiene (1,3-HCBD)	1.37	0.84	
1,2,4-Trichlorobenzene (1,2,4-TCB)	1.51	1.79	
1,2,3-Trichlorobenzene (1,2,3-TCB)	2.00	2.66	
Hexachlorocyclopentadiene (HCCP)	3.07		
1,2,3,5-Tetrachlorobenzene (1,2,3,5-TCB)	3.74		
1,2,4,5-Tetrachlorobenzene (1,2,4,5-TCB)	3.88		
1,2,3,4-Tetrachlorobenzene (1,2,3,4-TCB)	5.53		
α,α-2,6-Tetrachlorotoluene (α,α-2,6-TCT)	11.1		
Pentachlorobenzene (Penta CB)	12.4		

The results of Category III, Method B analyses for semi-volatile organochlorine compound residues in field samples are presented in Table V while those in volunteer samples are presented in Table VI. Table VII presents a summary of Tables V and VI results.

Fortification-recovery studies for Category III, Method B representative chemicals were conducted at low and high levels (about 1 and 10 ng/g or as otherwise indicated in Table VIII) as outlined for Category III, Method A chemicals above. The average percent recoveries of the low level samples were all higher than the high level samples, seven of them significantly higher ($p = 0.1$) using a t-test comparison. Thus, unlike Category III, Method A, the bias and precision of Category III, Method B, is concentration dependent at the levels studied. However, because the magnitude of the bias is small, an overall average percent recovery for each compound in Table VIII was calculated and used to correct the corresponding residue levels presented in Tables V, VI, and VII. The recovery of HCCP through the method was very low (about 4%), indicating that either this compound is not stable in whole blood or it cannot be accurately measured by this method of analysis.

Category III, Method C (GC/MS)

Twelve field and volunteer samples, selected because they exhibited high levels of specific residues by GC/EC analysis, were analyzed by gas chromatography/mass spectrometry (GC/MS). The entire contents of individual samples were weighed (7 to 10 g) and extracted using a scaled up version of the Category III, Method A procedure. Extracts were concentrated to approximately 40 µl and the entire sample subjected to GC/MS temperature programmed analysis with the MS operated at full gain in scanning mode.

Only one sample was analyzed in selected ion mode. All of the samples analyzed, including reagent blanks, contained various phthalate esters. Blood samples contained either butylated hydroxyanisole or butylated hydroxytoluene, "BD-Vacutainer contaminant" (tris-2-butoxyethylphosphate), 3,5-cholestadiene, cholesterol, and lesser amounts of other steroids. The organochlorine compounds detected in the whole blood samples analyzed are summarized in Table IX.

External standard solutions containing aminobenzotrifluoride, 3-chlorobenzoic acid methyl ester, and 4-chlorobenzoic acid methyl ester, compounds not detected by Category III, Method A or B (GC/EC) analyses, were analyzed by GC/MS analysis; if present in the samples analyzed, they would have been readily detected at levels of about 2, 1, or 1 ng/g (ppb), respectively. However, recovery studies for these compounds through the entire method were not performed and their analysis by HPLC/MS is only qualitative in nature. ACB sample numbers 001, 015, 016, 026, 032, and 036 as well as ACB control samples A and E were specifically analyzed for residues of these along with other compounds but none were detected. ACB sample number 029 was analyzed in selected ion monitoring mode where none but these specific compounds would have been detected.

External standard injections of the other standards in Category III were analyzed in scanning ion mode to determine the limits of detection of the GC/MS method. They were found to be in the range of 1 to 10 ng/g (ppb) with normal day-to-day fluctuations in sensitivity noticed. In addition, recovery studies were carried out by pooling four of the five low level (about 1 ng/g) fortified sample extracts of Tables IV and

VIII, after they had been analyzed by GC/EC. The average amount of each compound found by GC/EC analysis was used to calculate the theoretical amount injected for GC/MS analysis after concentration, as shown in Chart C. This qualitative experiment shows that most organochlorine compounds could be detected by the GC/MS method even when present at 1 ng/g (ppb) levels. Therefore, the absence of organochlorine compound residues reported for those samples analyzed by GC/MS (Table X) are confirmed at 1 to 10 ng/g (ppb) levels, as was indicated by the limits of detection for the method.

Category IV, Method A (HPLC/ECD)

The method reported by E. M. Lores, F. C. Meekins, and R. F. Moseman, J. Chromatogr. 188, 412-416 (1980) for the determination of halogenated anilines in urine by high-performance liquid chromatography with an electrochemical detector (HPLC/ECD) was modified and used for analysis of chlorophenol residues in blood. Whole blood samples (3-7 g) were hydrolyzed in dilute hydrochloric acid solution before the phenolic compounds were extracted into 1:1 (v/v) hexane/ethyl ether. The organic extracts were then partitioned with sodium hydroxide solution and the aqueous alkaline solutions containing the phenols were buffered by addition of phosphoric acid before portions were analyzed by HPLC/ECD under isocratic elution conditions.

The response and instrumental noise level of the electrochemical detector varied slightly from day to day so that a fixed limit of measurement cannot be quoted for the method. Instead, the limit of detection for the instrument was defined as the response of each phenol analyzed required to produce a signal to noise ratio of five; usually it was at 5 ng injected.

CHART C

GC/MS Confirmational Analysis of Fortified Control Whole Blood Samples

Compound	Amount injected (ng)	Confirmation result
1,3-DCB	10	No
1,4-DCB	12	No
1,2-DCB	9	No
2,4-DCT	10	No
1,3,5-TCB	12	Yes[a]
1,3-HCBD	10	Yes
1,2,3-TCB	11	Yes[a]
HCCP	0.7	No
1,2,4,5-TCB	11	Yes[a]
1,2,3,4-TCB	10	Yes[a]
Penta CB	10	Yes
HCB	7	Yes
γ-BHC	6	Yes[a]
PCNB	6	No
β-BHC	15	Yes[a]
Aldrin	6	No
Heptachlor epoxide	8	Yes
Oxychlordane	11	Yes
trans-Nonachlor	7	Yes
Thiodan II	4	No
Mirex	231	Yes

[a]The presence of one or both of the isomer pairs indicated was confirmed; a more definitive identification was not possible under the GC/MS temperature programmed conditions used.

The results of analysis of field and volunteer samples for levels of 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,4,5-trichlorophenol (2,4,5-TCP), and pentachlorophenol (PCP) are presented in Tables X and XI and summarized in Table XII. The HPLC/ECD chromatograms exhibited few extraneous peaks, except in the region of phenol and 2-chlorophenol (2-CP) which could not be analyzed using this method.

Fortification-recovery experiments were carried out at both low and high fortification levels (about 10 and 100 ng/g, respectively) as shown in Table XIII. No definitive trend in recovery towards concentration dependency was observed and the overall average percent recovery calculated for each compound was used to correct the corresponding residue levels found in the samples as discussed under the Category III, Method A section above.

Category IV, Method B (HPLC/MS)

Each aqueous acid sample remaining after HPLC/ECD analysis was partitioned with isooctane (2,2,4-trimethylpentane) to extract phenol, chlorophenols, and chlorobenzoic acids. An internal standard of p,p'-DDT was added to the organic phase which was then concentrated under a stream of dry nitrogen to 0.1 mL for high-performance liquid chromatographic/mass spectrometric (HPLC/MS) analysis. Aliquots (50 µL) were injected onto a LiChrosorb Diol column (3.2 mm i.d. x 25 cm) and eluted with a hexane/2-propanol mobile phase gradient at 1.8 mL/min. Mass spectral data was collected by scanning the 90 to 300 amu range using methane chemical ionization.

Limits of detection of the HPLC/MS system for chlorophenols and chlorobenzoic acids were determined by analysis of external reference standards. Day-to-day variations in instrument performance were observed, but under the conditions prevailing for most of the sample analyses, the limits of detection were approximately 40 ng injected.

No residues of monochlorobenzoic acids, dichlorobenzoic acids, monochlorophenols, or trichlorophenols were detected in any of the field samples analyzed by HPLC/MS. Residues of PCP were confirmed in 27 of the 35 field samples analyzed as shown in Table X. Residues (2 and 5 ng/g) of a dichlorophenol (either 2,3-; 2,4; or 2,5-DCP) were detected in 2 of 35 field samples. While residues of phenol ranging from 5 to 45 ng/g were found in 4 samples, their significance is in doubt since contamination of reagent blanks with phenol ranged from 5 to 56 ng/g.

In order to validate the recovery of chlorophenols through the HPLC/MS method, two volunteer blood samples were fortified at about 25 ng/g (ppb) with the mixture of compounds shown in Table XIII plus 2-chlorophenol. The recovery of PCP through the entire method averaged 80%. The recovery of 2,4-DCP averaged 30%, but the mono- and trichlorophenols were not recovered through the HPLC/MS method. It is possible that the lower chlorinated phenols were lost during the extraction and/or concentration steps. If they were injected into the HPLC/MS system, they would have been detected at the levels fortified. Recovery data was not obtained for phenol or the mono- and dichlorobenzoic acids.

For PCP, the results of the HPLC/MS analyses (Category IV, Method B) do confirm those obtained by HPLC/ECD (Category IV, Method A), and are reported in Table X. However, the indicated recovery problems with

the lower chlorinated phenols and the lack of recovery data for phenol, the monochlorobenzoic acids, and the dichlorobenzoic acids preclude the use of HPLC/MS analysis for definitive confirmation or analysis of these compounds at this time. Further recovery studies would be needed to accomplish this.

STATISTICAL ANALYSES

Statistical comparisons were made on the levels of chemical residues found in field and volunteer whole blood samples for compounds in Category III, Method A; Category III, Method B, and Category IV, Method A (Table XIV). Because the majority of these samples are below the minimum detectable level, comparisons are based on the number of positive (value above minimum detectable) tests found in each group. All of the comparisons were made using Fisher's Exact One-tailed Test, except for HCB. For that particular compound, all values were above the minimum detectable level so that both a t-test comparison of mean levels and a nonparametric comparison of rankings of values were used. All tests were made at the $p = 0.1$ level of significance.

None of the compounds tested in Caregory III, Method A, showed higher proportions of positive tests in the field samples. Of all the compounds in Category III, Method B, only 1,4-DCB showed a significant difference ($p = 0.042$), with the field samples having a higher proportion of positive samples. For the compounds in Category IV, Method A, only 3-CP had a higher proportion of field samples with positive values ($p = 0.052$).

It should be noted that these same comparisons were carried out comparing the field samples to the Analytical Chemistry Branch volunteers only and also to the student volunteers only, with less significant results always resulting from each of these comparisons when compared to the combined volunteer test results. This is to be expected since the sample sizes used for comparisons are accordingly reduced.

For HCB, the t-test comparison of means was marginally significant ($p = 0.097$) at the 0.1 level. The more robust Wilcoxon Rank Sum Test was also significant ($p = 0.02$), indicating higher relative rankings of field sample values versus volunteer sample values.

Percent recoveries for the above three categories of compounds were all compared using a t-test, again testing at the 0.1 level of significance. For Category III, Method A, compounds, β-BHC showed higher percent recoveries in the low dose group, whereas the reverse was true for PCNB. All others showed no significant differences. The Category III, Method B, compounds all showed significantly higher recoveries in the low dose group with the exception of 1,2-DCB, 2,4-DCT, and Penta CB where no differences were found. In Category IV, Method A, 2,4,5-TCP and 3-CP were the only compounds showing significantly different recoveries, again being higher in the low dose group.

In making multiple tests of significance as done in this report, one must always be aware that if k independent comparisons are done, each at the 0.1 level, the probability of one or more significant results, even when there are no treatment differences, equals $1 - (0.90)^k$.

DISCUSSION

A few comments regarding the results presented in this report are in order. In general, the literature contains little information about methods for analysis of and levels of the Category III and IV chemicals in blood. Because of this, the results reported herein must be interpreted with caution. Volunteer blood samples from local donors were collected and analyzed both to validate the methods described above and to provide an indication of background matrix effects normally encountered and limits of measurement that could be achieved.

The methods employed to analyze for chemical residues in whole blood are indicated in Appendix I. The Category III, Methods A and B, and Category IV, Method A, recoveries averaged about as expected except for Mirex and HCCP. Reference standards for all chlorobenzene and chlorotoluene isomers were not available. Gas chromatograms of the blood samples analyzed exhibited many low level responses, but enough standards were available to us to conclude that significantly high levels of chlorobenzene or chlorotoluene isomers not included in Tables I and V were not present above low ng/g (ppb) levels. All blood samples contained high levels of p,p'-DDE and levels of PCB that were generally at one-half of our limit of measurement for Aroclor 1260.

Residues of aminobenzotrifluoride and the chlorobenzoic acid methyl esters in whole blood could only have been detected by the Category IV, Method C procedure. None were detected in seven field and two volunteer samples analyzed, but the entire method has not been validated by fortification-recovery studies.

Although no residues of the mono- and dichlorobenzoic acid isomers were detected by the Category IV, Method B procedure, the entire method has not been validated by fortification-recovery studies. This method was validated for complete recovery of PCP, but only partial recovery of 2,4-DCP, and was used to positively confirm these residues in samples analyzed by HPLC/ECD (Table X). It did not appear to be valid for the mono- or trichlorophenols studied. Phenol and 2-chlorophenol could be detected but not measured in samples by either of the Category IV methods employed because of coeluting interferences. For details of the results of analysis of the Category I and II elements and chemicals performed by the Midwest Research Institute, see the attached report.

In general, we have conducted the analyses of Category III and IV compounds with considerable care both because the analyses utilize nonroutine methods or adapt routine methods and because the levels encountered have proved to be very low. The sensitivity of Category III analyses has been limited by reagent and sample background matrix effects, that of Category IV by instrumental noise and response factors. For these reasons, we feel that the fortification-recovery experiments and the MS confirmational analyses performed at low ng/g (PPB) levels were especially needed in order to validate the quantitative accuracy and qualitative significance of the residue levels reported for the samples analyzed.

In summary, a variety of elements and chemicals were sought in samples of whole blood obtained from 36 Love Canal area residents. The several analytical methods indicated in Appendix I were utilized in this endeavor. In order to conduct method trial and validation studies for

Category III and IV chemicals, the ACB obtained and analyzed volunteer samples from local donors of unknown exposure history. The volunteer samples do not and were not intended to represent closely matched control samples. Nevertheless, statistical analyses of differences between the residue levels of chemicals found in the field and volunteer samples were conducted. Some statistically significant differences ($p = 0.10$) were found; however, lacking meaningful control or literature data relative to the significance of the low residues of Categories III and IV chemicals found in the blood of the field samples analyzed, no definitive conclusions can be drawn from the results reported herein. Further analyses, including samples from a closely matched, simultaneous control group, would be needed to better define the utility of exposure assessment using these chemical measurements because the residue levels encountered by this study were very low.

APPENDIX I

List of Chemicals Analyzed by Method Employed

Category I, AAS[a]

Antimony
Arsenic
Cadmium
Chromium
Lead
Mercury
Nickel
Zinc

Category II, P&T-GC/MS[b]

Carbon tetrachloride
Chlorobenzene
Chloroform
Chlorotoluene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichloroethane
1,1-Dichloroethene
1,2-Dichloroethene (trans)
Tetrachloroethylene
Trichloroethylene

Category III, Method A

Hexachlorobenzene
α-Hexachlorocyclohexane (α-BHC)
β-Hexachlorocyclohexane (β-BHC)
δ-Hexachlorocyclohexane (δ-BHC)
γ-Hexachlorocyclohexane (γ-BHC)
Mirex
Pentachloronitrobenzene
Polychlorinated biphenyl (Aroclor 1260)
Thiodan I
Thiodan II

Category III, Method B

Benzyl chloride (α-Chlorotoluene)
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
2,4-Dichlorotoluene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Pentachlorobenzene
1,2,3,4-Tetrachlorobenzene
1,2,3,5-Tetrachlorobenzene
1,2,4,5-Tetrachlorobenzene
α,α,2,6-Tetrachlorotoluene
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,3,5-Trichlorobenzene

Category III, Method C

All chemicals in Category III, Methods A and B plus:
Aminobenzotrifluoride (α,α,α,-trifluoro-m-toluidine)
3-Chlorobenzoic acid methyl ester
4-chlorobenzoic acid methyl ester
Additional chemicals present (see text)

Category IV, Method A

3-Chlorophenol
4-Chlorophenol
2,4-Dichlorophenol
Pentachlorophenol
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol

Category IV, Method B

All dichlorobenzoic acid isomers (6)
All chlorobenzoic acid isomers (3)
2,4-Dichlorophenol
Pentachlorophenol

[a]Atomic absorption spectroscopy using hydride generation, graphite furnace, and flame atomization.

[b]Purge and trap GC/MS technique for analysis of volatile organic chemicals.

Table I. Category III, Method A (GC/EC-200°): Organochlorine Compound Residues in Whole Blood of Field Samples, ng/g (PPB)[a]

Compound:[b] / Limit of measurement:[c]			HCB 0.011	α-BHC[d] 0.047	γ-BHC 0.068	PCNB 0.15	β-BHC 0.21	δ-BHC 0.12	Thiodan I 0.23	Thiodan II 0.32	Mirex 0.22	Aroclor 1260 4.4
ACB number 119-	Field number	Sample weight (g)										
001	B14	2.05	0.4	NA[e]	-[f]	-	-	-	-	-	-	-
002	B19	2.28	0.4	NA	-	-	-	-	-	-	-	-
003	B20	2.06	0.6	-	-	-	0.4	-	-	-	-	-
004	B23	2.01	0.4	NA	-	-	0.4	-	-	-	-	-
005	B24	2.11	0.4	NA	-	-	-	-	-	-	-	-
006	B22	1.97	0.4	NA	-	-	-	-	-	-	-	-
007	B16	2.21	0.2	-	-	-	-	-	-	-	-	-
008	B25	1.87	0.3	NA	-	-	0.5	-	-	-	-	-
009	B15	1.96	1	-	-	-	-	-	-	-	-	-
010	B26	2.14	0.3	-	-	-	-	-	-	-	-	-
011	B17	1.84	0.1	NA	(i)[g]	-	-	-	-	-	-	-
012	B21	1.80	0.1	NA	-	-	-	-	-	-	-	-
013	B18	1.85	0.5	NA	-	-	0.2	-	-	-	-	-
014	B27	1.92	0.1	NA	-	-	-	-	-	-	-	-
015	B28	2.80	0.6	NA	-	-	0.4	-	(i)	-	-	-
016	B29	3.02	0.4	-	-	-	0.4	-	-	-	-	-
017	B31	3.11	0.3	-	-	-	0.2	-	-	-	-	-
018	B32	3.14	0.4	NA	(i)	(i)	(i)	(i)	(i)	-	(i)	-
019	B30	3.22	0.1	NA	NA	-	-	-	-	-	-	-
020	B35	2.83	(i)	NA	(i)	-	(i)	(i)	-	-	-	-
021	B33	2.99	0.3	-	-	-	0.4	-	-	-	-	-
022	B34	3.01	0.4	-	0.1	-	-	0.1	-	-	-	-
023	B36	3.42	3	NA	-	0.2	0.2	0.2	-	-	-	-
024	B37	3.85	0.6	NA	0.2	-	0.3	-	-	-	-	-
025	B38	3.59	0.6	NA	-	-	-	-	-	-	-	-
026	B39	3.33	0.4	-	0.2	-	0.2	-	-	-	-	-
027	B41	3.45	0.8	NA	0.1	-	-	-	-	-	-	-
028	B40	3.49	0.4	-	-	-	-	-	-	-	-	-
029	B43	3.22	0.8	-	0.2	-	0.3	-	-	-	-	-
030	B42	3.42	0.6	NA	-	-	-	-	-	-	-	-

Table I. (continued) Category III, Method A (GC/EC-200°): Organochlorine Compound Residues in Whole Blood of Field Samples, ng/g (PPB)[a]

Compound:[b] Limit of measurement:[c]			HCB 0.011	α-BHC 0.047	γ-BHC 0.068	PCNB 0.15	β-BHC 0.21	δ-BHC 0.12	Thiodan I 0.23	Thiodan II 0.32	Mirex 0.22	Aroclor 1260 4.4
ACB number 119-	Field number	Sample weight (g)										
031	B44	3.37	0.6	NA	-	-	0.2	0.2	-	-	-	8
032	B45	3.31	1	NA	-	-	0.4	-	-	-	-	-
033	B47	3.47	1	-	0.6	-	0.6	-	-	-	-	-
034	B46	3.24	0.3	NA	-	-	0.3	-	-	-	-	-
035	B48	3.16	0.6	-	-	-	0.3	-	-	-	-	-
036	B49	3.33	1	-	-	-	-	-	-	-	-	-

[a]Results are corrected for recovery except for Aroclor 1260.

[b]Text contains key to abbreviations used.

[c]Limit of measurement is in ng/g and represents the amount of each compound required to give a 10% full-scale recorder deflection under the conditions of analysis employed.

[d]Only selected samples were analyzed on the OV-17/OV-210 column at 175° to confirm α-BHC in the presence of HCB.

[e]NA indicates not analyzed.

[f]Dash indicates not present at the limit of measurement of the method.

[g]Interference present indicated by (i).

Table II. Category III, Method A (GC/EC-200°): Organochlorine Compound Residues in Whole Blood of Volunteer Samples, ng/g (PPB)[a]

Compound:[b] / Limit of measurement:[c]		HCB 0.011	α-BHC 0.047	γ-BHC 0.068	PCNB 0.15	β-BHC 0.21	δ-BHC 0.12	Thiodan I 0.23	Thiodan II 0.32	Mirex 0.22	Aroclor 1260 4.4
Volunteer sample	Sample weight (g)										
A[d]	3.10	0.3	NA[e]	-[f]	-	1	0.5	-	-	-	-
B	3.44	0.3	-	-	-	0.2	-	-	-	-	-
C	2.88	0.3	NA	-	-	-	-	-	-	-	-
D	3.07	0.3	NA	-	-	-	-	-	-	-	-
E	3.64	0.3	NA	-	-	0.5	-	-	-	-	-
F	3.20	0.4	NA	(i)[g]	(i)	(i)	-	-	-	-	-
G	3.00	0.4	NA	-	-	-	-	-	-	-	-
H	2.62	0.1	NA	-	-	-	-	-	-	-	-
I	1.94	0.3	0.1	0.1	-	0.6	-	-	-	-	-
J[d]	----	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
K[d]	3.25	1	NA	0.2	-	0.2	-	-	-	-	-
L[d]	3.41	0.2	NA	0.2	-	-	-	-	-	-	-
M[d]	2.99	0.2	NA	0.3	-	0.2	-	-	-	-	-

[a]Results are corrected for recovery.

[b]Text contains key to abbreviations used.

[c]Limit of measurement is in ng/g and represents the amount of each compound required to give a 10% full-scale recorder deflection under the conditions of analysis employed.

[d]Analyzed on one GC column only; not confirmed; results reported may be high.

[e]NA indicates not analyzed.

[f]A dash indicates not present at the limit of measurement of the method.

[g]Interference present indicated by (i).

Table III. Summary of Category III, Method A (GC/EC-200°) Results

		HCB	α-BHC[a]	γ-BHC	PCNB	β-BHC	δ-BHC	Thiodan I	Thiodan II	Mirex	Aroclor 1260
Number of samples analyzed[b]	Field	35	14	33	35	34	33	35	36	35	36
	Volunteer	12	2	11	11	11	12	12	12	12	12
Percentage positive	Field	100	0	21	3	50	9	0	0	0	3
	Volunteer	100	50	36	0	55	8	0	0	0	0
Mean of positive samples[c]	Field	0.6	0.0	0.2	0.2	0.3	0.2	0.0	0.0	0.0	8
	Volunteer	0.3	0.1	0.2	0.0	0.5	0.5	0.0	0.0	0.0	0
Range of positive samples[c]	Field	0.1-3	0.0	0.1-0.6	0.2	0.2-0.6	0.1-0.2	0.0	0.0	0.0	8
	Volunteer	0.1-1	0.1	0.1-0.3	0.0	0.2-1	0.5	0.0	0.0	0.0	0

[a] Only selected samples were analyzed on the OV-17/OV-210 column at 175° to confirm α-BHC in the presence of HCB.
[b] Samples exhibiting interferences are not included.
[c] In ng/g (PPB).

Table IV. Category III, Method A (GC/EC-200°): Recoveries of Organochlorine Compound Standards Added to Whole Blood[a,b]

Sample	HCB	γ-BHC	PCNB	β-BHC	Aldrin	Heptachlor epoxide	Oxy-chlordane	trans-Nonachlor	Thiodar II	Mirex
ACB pooled blood	-[c]	-	-	-	-	-	-	-	-	-
ACB pooled blood, low level fortification amounts found 1	(i)[e]	1.23	1.48	3.02	1.31	1.57	2.28	1.42	0.80	6.3
2	1.94	1.57	1.53	3.54	2.00	2.38	2.97	2.02	1.34	3.4
3	1.77	1.77	1.50	4.69	1.50	2.06	2.72	1.66	0.77	6.4
4	1.92	1.78	1.38	4.24	1.75	2.02	2.75	1.64	0.99	4.2
5	1.21	1.15	1.27	3.23	1.32	1.66	2.43	1.44	1.14	6.4
Average amount found	1.71	1.50	1.43	3.74	1.58	1.94	2.63	1.64	1.01	5.3
Amount added	2.45	1.70	1.77	3.48	3.00	3.00	3.00	3.00	1.35	15.2
Average percent recovery	69.8	88.2	80.9	108	52.5	64.6	87.7	54.5	74.7	35.1
RSD[d]	20.0	19.8	7.4	18.7	18.8	16.9	10.4	14.8	23.7	26.9
ACB pooled blood, high level fortification amounts found 1	20.3	18.2	16.6	35.1	16.2	22.5	32.4	19.5	14.3	47.1
2	16.7	14.1	19.4	27.5	12.0	17.7	25.5	15.3	11.9	76.0
3	18.1	15.0	14.5	28.5	16.2	20.4	26.7	17.4	11.9	51.7
4	17.4	15.5	18.0	29.9	14.4	18.6	27.6	16.2	12.8	58.7
5	17.4	14.4	18.0	27.1	14.4	19.2	26.4	17.1	11.1	51.2
Average amount found	18.0	15.4	17.3	29.6	14.6	19.7	27.7	17.1	12.4	56.9
Amount added	24.5	17.0	17.7	34.8	30.0	30.0	30.0	30.0	13.5	152
Average percent recovery	73.4	90.8	97.7	85.1	48.8	65.6	92.4	57.0	91.9	37.5
RSD	7.7	10.6	10.7	11.0	11.8	9.4	9.8	9.2	9.8	20.1
Overall average percent recovery (N = 10)	71.8	89.5	89.3	96.4	50.7	65.1	90.0	55.8	83.3	36.3
RSD	13.4	14.9	13.4	19.7	15.6	12.9	9.9	11.7	19.3	22.4

[a] ACB volunteer blood samples K, L, and M were pooled and analyzed to give the values indicated.
[b] Fortified blood samples weighed from 2.8 to 3.2 g (3.0 g average) and the amounts of organochlorine compounds added and found are given in ng.
[c] A dash indicates not present at the limit of measurement for the method.
[d] RSD = relative standard deviation (coefficient of variation).
[e] Coeluting interferences prevented accurate measurement of HCB.

Table V. Category III, Method B (GC/EC-100°): Organochlorine Compound Residues in Whole Blood of Field Samples, ng/g (PPB)[a]

Compound:[b] / Limit of measurement:[c]			1,3-DCB 0.97	1,4-DCB 1.6	α-CT 1.9	1,2-DCB 1.1	2,4-DCT 2.6	1,3,5-TCB 0.28	1,3-HCBD 0.088	1,2,4-TCB 0.46	1,2,3-TCB 0.37	HCCP 0.056	1,2,3,5-TCB 0.38	1,2,4,5-TCB 0.79	1,2,3,4-TCB 0.64	α,α,2,6-TCT 1.4	Penta CB 0.88
ACB number 119-	Field number	Sample weight (g)															
001	B14	2.05	-[d]	-	-	3	-	-	-	-	-	-	-	-	-	-	-
002	B19	2.28	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
003	B20	2.06	-	-	-	3	-	-	-	-	-	-	-	-	-	-	-
004	B23	2.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
005	B24	2.11	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
006	B22	1.97	-	-	-	3[e]	-	-	-	-	-	-	-	-	-	-	-
007	B16	2.21	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
008	B25	1.87	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
009	B15	1.96	-	2	-	-	-	-	-	-	-	-	-	-	-	-	-
010	B26	2.14	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
011	B17	1.84	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
012	B21	1.80	-	-	-	4	-	-	-	-	-	-	-	-	-	-	-
013	B18	1.85	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
014	B27	1.92	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
015	B28	2.80	7[f]	6[f]	-	4[f]	-	-	-	-	-	-	-	-	-	-	-
016	B29	3.02	7	20	-	4	-	-	-	-	-	-	-	-	-	-	-
017	B31	3.11	-	2	-	-	-	-	-	-	-	-	-	-	-	-	-
018	B32	3.14	8[e]	2	-	1	-	-	-	-	-	-	-	-	-	-	-
019	B30	3.22	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
020	B35	2.83	5[f]	7[f]	-	-	-	-	-	-	-	-	-	-	-	-	-
021	B33	2.99	3	5	-	3	-	-	-	-	-	-	-	-	-	-	-
022	B34	3.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
023	B36	3.42	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
024	B37	3.85	-	4	-	-	-	0.7	-	-	-	-	-	-	-	-	-
025	B38	3.59	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
026	B39	3.33	-	4	-	-	-	-	-	-	-	-	-	-	-	-	-
027	B41	3.45	3	2	-	-	-	-	-	-	-	-	-	-	-	-	-
028	B40	3.49	3	4	-	-	-	-	-	-	-	-	-	-	-	-	-
029	B43	3.22	-	21	-	-	-	-	-	-	-	-	-	-	-	-	-
030	B42	3.42	-	26	-	-	-	-	-	-	-	-	-	-	-	-	-

Table V. (continued) Category III, Method B (GC/EC-100°): Organochlorine Compound Residues in Whole Blood of Field Samples, ng/g (PPB)[a]

Compound:[b] / Limit of measurement:[c]			1,3-DCB 0.97	1,4-DCB 1.6	α-CT 1.9	1,2-DCB 1.1	2,4-DCT 2.6	1,3,5-TCB 0.28	1,3-HCBD 0.088	1,2,4-TCB 0.46	1,2,3-TCB 0.37	HCCP 0.056	1,2,3,5-TCB 0.38	1,2,4,5-TCB 0.79	1,2,3,4-TCB 0.64	α,α,2,6-TCT 1.4	Penta CB 0.88
ACB number 119-	Field number	Sample weight (g)															
031	B44	3.37	-	4	-	-	-	-	-	-	-	-	-	-	-	-	
032	B45	3.31	-	2	-	3	-	-	-	-	-	-	-	-	-	-	
033	B47	3.47	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
034	B46	3.24	-	2	-	-	-	-	-	-	-	-	-	-	-	-	
035	B48	3.16	-	2	-	-	-	-	-	-	-	-	-	-	-	-	
036	B49	3.33	-	2	-	-	-	-	-	-	-	-	-	2	-	-	

[a] Results are corrected for recovery.

[b] Text contains key to abbreviations used.

[c] Limit of measurement is in ng/g and represents the amount of each compound required to give a 10% full-scale recorder deflection under the conditions of analysis employed.

[d] A dash indicates not present at the limit of measurement of the method.

[e] Presence not confirmed by analysis on a second GC column, may represent a false positive.

[f] Sample not available for analysis on second GC column.

Table VI. Category III, Method B (BC/EC-100°): Organochlorine Compound Residues in Whole Blood of Volunteer Samples, ng/g (PPB)[a]

Compound:[b] / Limit of measurement:[c]		1,3-DCB 0.97	1,4-DCB 1.6	α-CT 1.9	1,2-DCB 1.1	2,4-DCT 2.6	1,3,5-TCB 0.28	1,3-HCBD 0.088	1,2,4-TCB 0.46	1,2,3-TCB 0.37	HCCP 0.056	1,2,3,5-TCB 0.38	1,2,4,5-TCB 0.79	1,2,3,4-TCB 0.64	α,α,2,6-TCT 1.4	Penta CB 0.88
Volunteer sample	Sample weight (g)															
A	3.10	-[d]	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	3.44	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	2.88	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	3.07	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E	3.64	9	9	-	4	-	-	-	-	-	-	-	-	-	-	-
F	3.20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
G	3.00	3	2	-	-	-	-	-	-	-	-	-	-	-	-	-
H	2.62	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
I	1.94	-	-	-	4	-	-	-	-	-	-	-	-	-	-	-
J	----	NA[e]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
K	3.25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
L	3.41	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
M	2.99	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

[a]Results are corrected for recovery.

[b]Text contains key to abbreviations used.

[c]Limit of measurement is in ng/g and represents the amount of each compound required to give a 10% full-scale recorder deflection under the conditions of analysis employed.

[d]A dash indicates not present at the limit of measurement of the method.

[e]NA indicates not analyzed.

Table VII. Summary of Category III, Method B (GC/EC-100°) Results

		1,3-DCB	1,4-DCB	α-CT	1,2-DCB	2,4-DCT	1,3,5-TCB	HCBD	1,2,4-TCB	1,2,3-TCB	HCCP	1,2,3,5-TCB	1,2,4,5-TCB	1,2,3,4-TCB	α,α,2,6-TCT	Penta CB
Number of samples analyzed	Field	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36
	Volunteer	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12
Percentage positive[a]	Field	20	50	0	25	0	3	0	0	0	0	0	3	0	0	0
	Volunteer	17	17	0	17	0	0	0	0	0	0	0	0	0	0	0
Mean of positive samples[b]	Field	5	7	-	3	-	0.7	-	-	-	-	-	2	-	-	-
	Volunteer	6	6	-	4	-	-	-	-	-	-	-	-	-	-	-
Range of positive samples[b]	Field	3-8	4-26	-	1-4	-	0.7	-	-	-	-	-	2	-	-	-
	Volunteer	3-8	2-9	-	4	-	-	-	-	-	-	-	-	-	-	-

[a] Excludes responses not observed when sample was analyzed on a second GC column.

[b] In ng/g (PPB).

Table VIII. Category III, Method B (GC/EC-100°): Recoveries of Organochlorine Compound Standards Added to Whole Blood[a,b]

Sample	1,3-DCB	1,4-DCB	1,2-DCB	2,4-DCT	1,3,5-TCB	1,3-HCBD	1,2,3-TCB	HCCP	1,2,4,5-TCB	1,2,3,4-TCT	Penta CB
ACB pooled blood	-[c]	-	-	-	-	-	-	-	-	-	-
ACB pooled blood, low level fortification amounts found 1	2.49	2.92	2.48	2.71	3.14	2.60	2.68	2.0	2.96	2.54	2.44
2	2.38	3.17	2.48	2.47	3.01	2.45	2.82	2.0	2.85	2.54	2.44
3	2.43	2.95	2.40	3.21	2.99	2.51	2.68	1.0	2.73	2.54	2.41
4	2.54	2.95	2.30	2.44	3.03	2.50	2.74	2.0	2.85	2.67	2.50
5	2.49	2.95	2.24	2.81	2.78	2.36	2.61	2.0	2.73	2.54	2.52
Average amount found	2.47	2.99	2.38	2.73	2.99	2.48	2.70	1.8	2.82	2.57	2.46
Amount added	3.10	3.40	2.98	3.00	3.20	3.15	3.06	32.4[e]	2.85	2.85	3.06
Average percent recovery	79.7	87.9	79.9	90.9	93.4	78.9	88.4	5.6	99.1	90.0	80.5
RSD[d]	2.5	3.5	4.6	11.4	4.4	3.5	3.0	24.8	3.5	2.3	2.0
ACB pooled blood, high level fortification amounts found 1	20.8	26.3	20.4	26.2	23.3	20.0	23.1	3.2	21.4	21.4	23.2
2	19.9	26.1	19.7	26.6	22.3	19.2	22.2	3.2	20.2	20.6	22.6
3	21.5	26.1	21.6	27.2	25.1	22.9	24.6	9.7	23.3	22.6	21.7
4	23.7	24.3	24.4	25.3	26.8	22.3	26.9	3.2	28.1	24.7	28.3
5	21.6	25.2	23.0	23.1	26.0	23.0	26.2	3.2	25.0	24.4	26.0
Average amount found	21.5	25.6	21.8	25.7	24.7	21.5	24.6	4.5	23.6	22.7	24.4
Amount added	31.0	34.0	29.8	30.0	32.0	31.5	30.6	324[e]	28.5	28.5	30.6
Average percent recovery	69.4	75.3	73.2	85.6	77.2	68.2	80.4	1.4	80.9	79.6	79.6
RSD	4.5	3.2	8.8	6.2	7.5	8.2	8.0	64.6	9.8	8.2	11.2
Overall average percent recovery (N = 10)	74.5	81.6	76.6	88.2	85.3	73.6	84.4	3.5	90.0	84.8	80.0
RSD	3.5	3.3	6.7	8.8	6.0	5.9	5.5	70.7	6.6	5.3	6.6

[a] ACB volunteer blood samples K, L, and M were pooled and analyzed to give the values indicated.
[b] Fortified blood samples weighed from 3.0 to 3.2 g (3.1 g average) and the amounts of organochlorine compounds added and found are given in ng.
[c] A dash indicates not present at the limit of measurement for the method.
[d] RSD = relative standard deviation (coefficient of variation).
[e] Samples were fortified with HCCP at about 11 or 110 ng/g because of the low recovery encountered.

Table IX. Category III, Method C (GC/MS): Confirmation of Organochlorine Compounds Found in Whole Blood of Selected Samples

ACB - 119 Sample Analyzed	Compounds Confirmed as Present[a]
001	DDE
007[b]	HCB
015	1,4-DCB, a trichlorobiphenyl isomer, heptachlor epoxide, trans-nonachlor, DDE, hexachlorobiphenyl isomers
016	DCB, HCB, a trichlorobiphenyl isomer, heptachlor epoxide, trans-nonachlor, a pentachlorobiphenyl isomer, DDE
023[b]	HCB
026	1,2-DCB, 1,3,5-TCB, HCB, a trichlorobiphenyl isomer
029[c]	none (selected ion monitoring mode)
032[c]	1,2-DCB, 1,2,4-TCB
033[d]	Two different tetrachlorobenzene isomers, pentachlorobenzene, HCB
036	1,3-DCB, 1,2,4,5-TCB
Volunteer A	HCB, heptachlor epoxide, trans-nonachlor, DDE, hexachlorobiphenyl isomers
Volunteer E	DCB, a trichlorobenzene isomer, HCB, tri-, tetra-, penta-, and hexachlorobiphenyl isomers, trans-nonachlor, DDE

[a] Samples were injected at or below 80° and temperature programmed at 8°/min to 240° or 300° unless noted otherwise. Isomer assignments are based on isothermal GC/EC relative retention times, not on GC/MS data.

[b] Run isothermally at 180° to give most sensitive detection possible for pesticides and PCB.

[c] Run isothermally at 80° to give most sensitive detection possible for aminobenzotrifluoride and monochlorobenzoic acid methyl ester isomers.

[d] Injected at 140° and temperature programmed at 8°/min to 240° to give most sensitive detection of tetra- and pentachlorobenzenes.

Table X. Category IV, Method A (HPLC/ECD): Chlorophenol Residues in Whole Blood of Field Samples, ng/g (PPB)[a]

ACB number 119-	Field Number	Sample weight (g)	3-CP	4-CP	2,4-DCP	2,4,6-TCP	2,4,5-TCP	PCP[b]
001	B14	3.80	-[c]	-	-	2	-	23
002	B19	3.43	-	-	-	-	-	-
003	B20	5.01	3	5	-	-	-	39
004	B23	4.93	-	-	-	-	3	19
005	B24	5.33	-	-	-	-	2	10
006	B22	4.06	-	-	-	-	3	22
007	B16	3.79	-	-	-	-	-	13
008	B25	3.48	48	73	-[d]	-[d]	-[d]	-[d]
009	B15	5.01	-	-	-[d]	4[d]	-[d]	33[d]
010	B26	5.20	-	15	-	-	-	32
011	B17	5.16	8	11	-	-	-	18
012	B21	5.43	9	25	-	-	-	9
013	B18	5.00	-	-	-	-	-	-
014	B27	5.98	-	-	-	-	-	16
015	B28	----[e]	NA	NA	NA	NA	NA	NA
016	B29	6.23	-	-	-	-	-	10
017	B31	5.10	1	-	-	-	-	5
018	B32	6.20	-	-	-	-	-	5
019	B30	6.07	9	3	-	-	-	10
020	B35	5.96	1	1	-	-	-	10
021	B33	5.36	31	90	-	-	-	14
022	B34	6.18	5	-	-	-	-	8
023	B36	6.34	39	-	-	-	-	9
024	B37	4.93	3	-	-	-	-	5
025	B38	6.16	-	-	-	-	-	18
026	B39	5.01	44	-	-	-	-	8
027	B41	5.40	6	-	-	-	-	5
028	B40	5.29	84	-	-	-	-	11

Table X (continued). Category IV, Method A (HPLC/ECD): Chlorophenol Residues in Whole Blood of Field Samples, ng/g (PPB)[a]

ACB number 119-	Field Number	Sample weight (g)	3-CP	4-CP	2,4-DCP	2,4,6-TCP	2,4,5-TCP	PCP[b]
029	B43	5.07	-	-	5	-	-	10
030	B42	5.51	17	58	-	-	-	5
031	B44	7.21	-	-	-	-	-	8
032	B45	5.11	-	-	-	-	-	10
033	B47	6.00	-	-	-	-	-	5
034	B46	6.59	2	10	-	-	-	18
035	B48	6.54	-	(i)[f]	-	-	-	8
036	B49	5.28	-	-	-	-	3	4

[a] Results are corrected for recovery.
[b] Presence or absence of PCP was confirmed by HPLC/MS analysis in all samples except ACB numbers 006, 007, 011, 026, 027, and 036.
[c] A dash indicates not present at the limit of detection which was set at a signal to noise ratio of 4.
[d] Presence or absence was confirmed by EC/GC analysis.
[e] NA indicates that sufficient sample was not available for analysis.
[f] A coeluting interference prevented accurate measurement.

Table XI. Category IV, Method A (HPLC/ECD): Chlorophenol Residues in Whole Blood of Volunteer Samples, ng/g (PPB)[a]

Volunteer Sample	Sample Weight (g)	3-CP	4-CP	2,4-DCP	2,4,6-TCP	2,4,5-TCP	PCP
A	5.84	-[b]	-	-	-	-	5
B	5.70	-	-	-	-	-	-
C	5.96	82	-	-	-	-	5
D	5.67	32	-	-	-	-	6
E	5.69	-	-	-	-	-	13
F	5.66	-	-	-	-	-	8
G	5.20	-	2	-	-	-	5
H	5.24	-	-	-	-	-	5
I	5.90	-	-	-	-	-	15
J	5.55	-	-	-	-	-	5
K	5.08	-	-	-	-	-	lost
L	5.00	-	-	-	-	-	8
M	5.15	-	-	-	-	-	3
Reagent blank	----	-	-	-	-	-	-

[a] Results are corrected for recovery.
[b] A dash indicates not present at the limit of detection for the method which was set at a signal to noise ratio of 4.

Table XII. Summary of Category IV, Method A (HPLC/ECD) Results

		3-CP	4-CP	2,4-DCP	2,4,6-TCP	2,4,5-TCP	PCP
Number of samples analyzed	Field	35	34	35	35	35	35
	Volunteer	13	13	13	13	13	12
Percentage positive	Field	46	29	3	6	11	91
	Volunteer	15	8	0	0	0	92
Mean of positive samples[a]	Field	19	29	5	3	3	13
	Volunteer	57	2	0	0	0	7
Range of positive samples[a]	Field	1-84	1-90	5	2-4	2-3	3-39
	Volunteer	32-82	2	0	0	0	3-15

[a]Values are in ng/g (PPB) and are corrected for recovery.

Table XIII. Category IV, Method A (HPLC/ECD): Recoveries of Chlorophenol Standards Added to Whole Blood[a,b]

Sample		3-CP	4-CP	2,4-DCP	2,4,6-TCP	2,4,5-TCP	PCP
ACB pooled blood		-[c]	-	-	-	-	3[d]
ACB pooled blood, low level fortification amounts found	1	36.2	44.2	47.3	36.2	52.6	80.0
	2	38.4	41.7	38.4	39.3	55.7	97.8
	3	42.3	48.3	46.5	34.5	46.9	56.6
	4	42.2	47.1	44.4	36.4	44.4	76.8
	5	43.7	36.7	46.2	38.2	52.2	115
Average amount found		40.6	43.6	44.6	36.9	50.4	85.3
Amount added		50.7	44.8	47.2	45.2	50.4	105
Average percent recovery		80	97	94	82	100	81
RSD[e]		6.2	11	8.1	5.1	9.1	26
ACB pooled blood, high level fortification amounts found	1	450	380	425	346	400	1008
	2	460	380	450	345	460	760
	3	649	428	428	391	438	695
	4	447	408	384	384	413	549
	5	440	419	393	419	450	1013
Average amount found		489	403	416	377	432	805
Amount added		507	448	472	452	504	1050
Average percent recovery		96	90	88	83	86	77
RSD		18	5.5	6.5	8.4	5.8	25
Overall average percent recovery (N=10)		88	94	91	83	93	79
RSD		17	9.2	7.9	6.7	11	24

[a]ACB volunteer samples K, L, and M were pooled and analyzed to give the values indicated.
[b]Fortified blood samples weighed from 4.5 to 5.5 g and the amounts of chlorophenols added and found are given in ng.
[c]A dash indicates not present at the limit of detection for the method which was set at a signal to noise ratio of 4.
[d]This value was used to correct the amounts found.
[e]RSD = relative standard deviation (coefficient of variation).